1 of 1

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**Permeation of Argon, Carbon Dioxide, Helium, Nitrogen and Oxygen
Through Mylar Windows***

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ABSTRACT

In secondary beam lines in the Alternating Gradient Synchrotron (AGS) at Brookhaven National Laboratory, low mass vacuum windows are used to reduce background radiation near particle detectors. These windows are fabricated using Mylar** films and are generally made as thin as possible. Mylar films as thin as 0.002" have been used as vacuum windows ranging in size up to 36" x 76". When using Mylar for low mass window applications, permeation must be considered to achieve system design pressures. The permeation of several different gas species through both Mylar and aluminized Mylar films with thicknesses of 0.002" and 0.005" has been studied. Testing was performed under high vacuum and a quadrupole mass spectrometer was used to identify and quantify gas species during the study. The permeability of Argon, Carbon Dioxide, Helium, Nitrogen and Oxygen were determined for Mylar from 20°C up to 90°C.

Introduction

At Brookhaven National Laboratory, Mylar is widely used for vacuum windows on experimental beam lines in the AGS complex. In some instances these windows are required to be as thin as possible in order to reduce background radiation as the beam passes through

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**Mylar is a registered trademark of Dupont.

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them. When using very thin windows, permeation must be considered when trying to achieve system design pressure. Since there is little published data for the permeation constants of various gasses through Mylar, it was decided to measure the permeation rates for Argon, Carbon Dioxide, Helium, Nitrogen and Oxygen through Mylar film. The permeation through a sample of commercially available aluminized Mylar was also investigated. The permeation constants were calculated from measured data as a function of pressure, as well as a function of temperature. A quadrupole mass spectrometer was used to measure the partial pressures inside the vacuum chamber and to verify that the system was at steady state.

Test Apparatus

A Mylar window was mounted on a vacuum chamber that was pumped via an orifice with a known conductance. On the other side of the orifice was a second chamber with a 300//s turbomolecular pump mounted as shown in Figure 1. Bayert-Alpert gauges (BAG) were placed in both chambers so that the flow rate of the gas that permeated through the window could be accurately calculated by measuring the pressure difference across the orifice. BAGs of the same type were previously calibrated at Brookhaven against a spinning rotor gauge [1]. An absolute pressure gauge was used to measure the pressure of the test gas chamber. This allowed accurate pressure measurement of the test gasses from atmosphere down to about 10 torr. A quadrupole type RGA was used above the orifice to measure the background, determine what gas species were present, and determine the relative abundance of the test gas.

The test chambers were assembled using 4" diameter stainless steel tube and 6" conflat flanges in order to eliminate any effects of permeation through non-metallic seals. The window itself was assembled by cutting a circular sheet of the Mylar film to the outside diameter of a conflat gasket and sandwiching it between two full thickness gaskets. The window aperture was

4.00". The joint sealed reliably, which avoided the need to use o-rings. The orifice diameter used was 0.250" for which the conductance was calculated for each test gas. A mechanical pump in conjunction with a throttle valve, was used to provide a vacuum on the test gas side of the Mylar film. Each gas was introduced into the chamber through a pressure regulator and a throttle valve. The throttle valves on the mechanical pump and the gas inlet were adjusted in order to accurately control the pressure of the test gas chamber.

Test Procedure

During the initial attempts to measure the permeation rates for the various gasses, both sides of the Mylar film were evacuated for about 36 hours in order to bring the background to equilibrium. RGA scans were taken periodically and used to establish when the system pressure was stable. Once the base pressure was established, the test gas was introduced into the test gas chamber side of the Mylar and the pressure was adjusted to give a constant 700 Torr pressure reading on the absolute pressure gauge. After taking repeated RGA scans over a period of time, a point where the partial pressure of the test gas peaks out and becomes constant could be established. This, along with establishing a constant pressure reading on the BAGs, allowed the measurement of the permeation rate as a function of pressure. However, it was discovered that the background needed to be reduced since the RGA scans indicated that the test gas was not the predominant gas species on the high vacuum side of the Mylar film. Since water vapor was the predominant gas, the chamber was baked to reduce the background pressure.

Baking the chamber presented a problem since Mylar loses considerable tensile strength at higher temperatures. The entire chamber was wrapped with heater tapes except for the conflat window flanges and about 1.5" above and below the window. Five thermocouples were placed at various locations on the window flanges and exposed tubing in order to monitor the Mylar

film temperature. The entire chamber was baked to 150°C except for the window area, which was held at about 50°C with the aid of a fan blowing room air on the flanges. Vacuum was maintained on both sides of the window during the bakeout so that the Mylar was not stressed while the window was at elevated temperatures. The chamber was baked for 48 hours along with a periodic degassing of the ion gauges and the RGA. When the chamber cooled to room temperature, the background pressure on the turbo side of the orifice plate was low 10^{-9} Torr while the pressure above the orifice plate was mid 10^{-8} Torr. The RGA scan indicated that the predominant gas species was hydrogen and that the partial pressure of hydrogen was about three and a half times as high as that of water vapor when a background scan was taken.

To measure the permeation rate as a function of pressure the background pressure was established as described above. Each test gas was introduced to the test gas chamber and throttled to maintain a constant pressure on the absolute pressure gauge. After some time, the pressure indicated by the BAGs on the high vacuum side of the Mylar film reached an equilibrium point where the total pressure readings did not change. At this point, RGA scans were taken to ensure that the partial pressure of the test gas had reached equilibrium. Once all the data was taken for that particular test gas pressure, the test gas pressure was decreased by 100 Torr. The test gas pressure for all gasses was varied from 700 Torr down to 100 Torr.

To measure the permeation rate through Mylar film as a function of temperature, the same test apparatus as mentioned previously was used. The procedure used was as follows. The pressure of the test gas chamber was held constant at about 700 Torr while heater tapes that were wrapped on the test gas chamber and the window flanges controlled the temperature of the window and the test gas chamber. The temperature of the window and test gas chamber was increased by 10°C increments from room temperature up to 90°C. After temperature equilibrium

was reached, measurements were taken for each test gas species. The equilibrium point was again established by monitoring the BAG readings and taking RGA scans.

The gasses tested and their purity are as follows Helium 99.998%, Argon 99.99%, Carbon Dioxide 99.98%, Nitrogen 99.999% and Oxygen 98.9%.

Calculations

To calculate the permeation rate of the test gasses, the indicated ion gauge pressures, as well as the conductances, for each gas must be calculated.

The conductances, C through the orifice plate were calculated for each test gas using the following formula.

$$C = 3.64K'A(T/M)^{1/2} \text{ l/s} \quad (1)$$

where K' = Clausing factor for a short tube/orifice

A = Area of aperture (cm^2)

T = room temperature (295°K)

M = Molecular weight of test gas

The ion gauge pressures on both side of the orifice were recorded when the equilibrium point was reached. These pressures were corrected for the corresponding test gas species by the following formula:

$$\Delta P' = \Delta P / K_1 \quad (2)$$

Where $\Delta P'$ = corrected ion gage pressure differential

$\Delta P = (P_3 - P_2)$ differential pressure across the orifice plate

K_1 = relative gauge sensitivity of test gas species

The gauge sensitivity factors used, as suggested by the gauge controller manufacturer, were 1.29, 1.42, 0.18, 1.0 and 1.01 for Argon, Carbon Dioxide, Helium, Nitrogen and Oxygen, respectively.

The rate of permeation, Q as a function of pressure, as well as temperature, was calculated by: $Q = \Delta P^1 \times C$. The rate of permeation can also be expressed as:

$$Q = K P_1 A / d \quad (3)$$

where Q = rate of permeation (sccm sec⁻¹)
 P_1 = pressure of test gas chamber (atm)
 A = window area (cm²)
 d = window thickness (cm)
 K = permeability (sccm cm⁻² cm sec⁻¹ atm⁻¹)

The test gas pressure P , was corrected for the gas density at elevated temperatures by using $(T_{295}/T_{\text{chamber}})^{1/2}$ as a correction factor since the absolute pressure gauge was at 295°K. For a window with a known area and thickness the permeability K can be derived from Q and P_1 using equation (3).

Since the permeability K increases with temperature, it is possible to express K as a function of T by the following expression [2].

$$K = K_o e^{-E/R_o T} \quad (4)$$

Where ΔE = activation energy for the permeation cal/mol.

K_o = Permeation constant (sccm cm⁻² cm sec⁻¹ atm⁻¹)

R = 1.987 cal/mol.°K

T = Temperature of window (°K).

By plotting and fitting the measured $\log K$ against temperature $1/T$, ΔE , and K_0 can be calculated as the slope and intercept of the fitted lines, respectively.

Test Results and Discussion

Figure 2 shows a comparison of the background RGA scan before and after bake of the test apparatus. After bake the Hydrogen peak was the predominant gas present and this was a typical background scan before each gas was introduced to the system. Figures 3 through 7 show a comparison of the RGA scans with the test gas chamber pressure at 100 and 700 Torr for each gas tested. Clearly from the scans of the inert test gasses such as Argon, Helium and Nitrogen (Figures 3,4 and 5, respectively) the test gas was the predominant gas species by a large factor. Figure 6, which is the RGA scan for Carbon Dioxide as the test gas, shows a typical cracking pattern for CO_2 . Figure 7 shows the scans of Oxygen as the test gas. The large peaks, such as H_2O , CO_2 , C and CO absent during the background scans were originated from chemical reactions of Oxygen with active surfaces. Therefore, in all the tests the contribution from background to the total pressure was negligible and gauge sensitivity factors for each gas were used to correct the total pressure readings indicated by the BAGs.

Figures 8 and 9 show a plot of the $\log K$ versus $1/T$ for all test gasses through 0.002" (0.0018" actual) Mylar. The lines drawn were a least square fit of $\log(K)$ vs $1/T$ of the test data points. From the slope and intercept of the line the activation energy ΔE and the permeation constant K_0 for each gas can be calculated. Once the activation energy and the permeation constant is determined the permeability can be calculated for any given temperature by using equation (4). The rate of permeation can then be estimated for any window with a known area, thickness, and gas pressure by using equation (3). Table 1 lists the activation energies and the permeation constants for each gas. The calculated permeability using ΔE , K_0

and equation (4) and the measured permeability at 22°C are given in Table 1 as a comparison. The measured permeability at 22°C are obtained from the weighted average of the K values obtained at various pressures, using rate of permeation Q, test gas chamber pressure P_1 and equation (3). The rate of permeation for different gasses are plotted versus pressure in Figures 10 through 12. The measured permeability are in reasonable agreement with the calculated values except for Oxygen. The large difference in the calculated K and the measured K for Oxygen may have been caused by surface reactions within the system during the tests.

Figure 13 shows a plot of $\log K$ versus $1/T$ for 0.005" (0.0042" actual) Mylar for Helium and Carbon Dioxide. The calculated activation energy and permeation constant are also given in Table 1. Large uncertainties resulted since there was not as many data points taken as compared to the test on the 0.0018" Mylar. The time necessary for the system to reach equilibrium after the temperature stabilized was also much longer than that of the test run with the 0.0018" Mylar. In the case of Helium as the test gas, even though ΔE and K_0 are different from those of 0.0018" Mylar, the calculated permeability K at 22°C was in agreement with that of the 0.0018" Mylar. In the case of Carbon Dioxide as the test gas the comparison of the calculated K of 0.0042" Mylar at 22°C was lower by a factor of 2 than that of 0.0018" Mylar. More study is planned to characterize the permeation of Argon, Nitrogen, and Oxygen through 0.0042" Mylar.

Several samples of commercially available aluminized Mylar which measured out to be .0018" thick were also tested. It was expected that there would be a substantial reduction in the permeation rate due to the aluminum coating. The plots of the rate of permeation Q versus absolute pressure for the aluminized Mylar are shown in Figures 10 and 11. The plots show that the rate of permeation for both CO_2 and He were slightly higher than that of plain Mylar. The

thickness of the aluminum deposited on the Mylar was on the order of about one micro-inch.

Since this result was unexpected, more study is needed to determine if the physical properties of the Mylar itself are exactly the same as that of the plain Mylar tested and if the metalizing process has any effect on the structure of Mylar.

Conclusion

The permeation data results from this study for Helium, Nitrogen, Carbon Dioxide and Oxygen at room temperature are very close to the data of polyimide Peacock [3] reported. By determining the activation energy and the permeation constant for Argon, Carbon Dioxide, Helium, Nitrogen and Oxygen the permeability through Mylar can be found at any temperature. The results from this data are very useful when performing calculations involving Mylar windows when permeation can be a limiting factor in achieving system design pressures. The use of aluminized Mylar to reduce the rate of permeation will be investigated in the future.

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Figure Caption:

Fig. 1 The experimental setup for measuring the gas permeation through thin Mylar.

Fig. 2 The background RGA scans before and after baking.

Fig. 3 The RGA scan of Argon as the test gas.

Fig. 4 The RGA scan of Helium as the test gas.

Fig. 5 The RGA scan of Nitrogen as the test gas.

Fig. 6 The RGA scan of Carbon Dioxide as the test gas.

Fig. 7 The RGA scan of Oxygen as the test gas.

Fig. 8 Permeability of Helium and CO₂ versus Temperature For 0.0018" Mylar, K (sccm cm⁻² cm sec⁻¹ atm⁻¹)

Fig. 9 Permeability of Argon, Nitrogen, and Oxygen versus Temperature for 0.0018" Mylar, K (sccm cm⁻² cm sec⁻¹ atm⁻¹)

Fig.10 Rate of Permeation versus Absolute Pressure for Helium

Fig.11 Rate of Permeation versus Absolute Pressure for CO₂

Fig.12 Rate of Permeation versus Absolute Pressure for O₂, Ar, and N₂

Fig.13 Permeability of Helium and CO₂ versus Temperature for 0.0042" Mylar

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TABLE 1

**SUMMARY OF ACTIVATION ENERGY, PERMEATION CONSTANT, AND
PERMEABILITY AT 22°C**

Gas	Thickness (MIL)	ΔE (K Cal/Mol)	$K_o (10^{-6})$ (sccm cm ⁻² cm sec ⁻¹ atm ⁻¹)	Calculated K (22°C)	Measured K (21-23°C)		
					1.8 MIL	Aluminized 1.8 MIL	4.2 MIL
He	1.8	5.0 ± 0.1	95 ± 12	1.9E-08	1.7E-08	2.0E-08	1.2E-08
	4.2	5.8 ± 0.4	375 ± 247	1.9E-08			
N ₂	1.8	7.1 ± 0.1	26 ± 5	1.4E-10	1.8E-10		
Ar	1.8	7.6 ± 0.1	134 ± 14	3.1E-10	2.8E-10	2.8E-10	
CO ₂	1.8	4.4 ± 0.2	8.9 ± 2.1	4.9E-09	3.7E-09	5.8E-09	3.0E-09
	4.2	4.6 ± 0.7	6.4 ± 4.1	2.5E-09			
O ₂	1.8	6.2 ± 0.1	31 ± 7	7.9E-10	8.5E-08

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5
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Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

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